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MEMORANDUM FOR PRS (In-House/Contractor Publication)

FROM: PROI (STINFO) 19 Apr 2001

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-AB-2001-103**
Jerry Boatz; Don Thompson and Dan Sorescu (Oklahoma State Univ.), "Bond Dissociation Energies of Energetic Compounds: A Comparison of Theoretical Methods"

AFOSR Contractors Meeting **(Statement A)**
(Irvine, CA, 21-23 May 2001) (Deadline: 18 May 01)

1. This request has been reviewed by the Foreign Disclosure Office for: a.) appropriateness of distribution statement, b.) military/national critical technology, c.) export controls or distribution restrictions, d.) appropriateness for release to a foreign nation, and e.) technical sensitivity and/or economic sensitivity.
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_____

PHILIP A. KESSEL Date
Technical Advisor
Space and Missile Propulsion Division

Bond Dissociation Energies of Energetic Compounds: A Comparison of Theoretical Methods

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AFOSR Molecular Dynamics/Theoretical Chemistry Contractors Conference
May 21-23, 2001
Irvine, CA

Outline

I. Overview of AFRL - Propulsion Directorate
   - High Energy Density Materials (HEDM) for rocket propulsion
   - Specific impulse as an assessment of energy density

II. C-N bond energies of 1,1-diamino-2,2-dinitroethylene ("FOX-7") and prototypes

III. Results

IV. Summary and Conclusions

Why is the Air Force interested in HEDM?

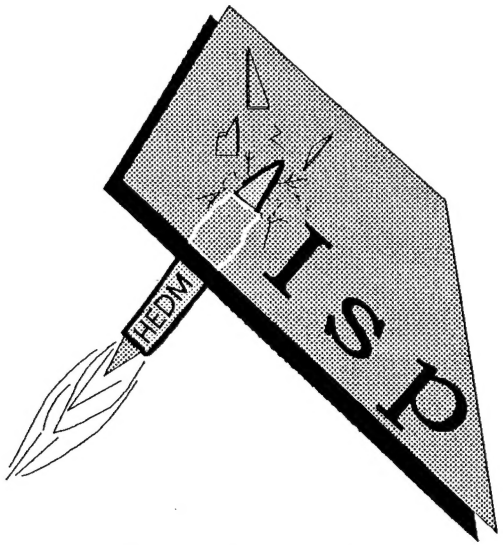
The performance limits of current propellants have been reached

- The constituents of current propellants have been known for decades
- New missions require higher-performing propulsion systems

A revolutionary propulsion source would substantially improve our ability to access and exploit space

- Fusion, antimatter, and beamed energy are tantalizing but distant prospects
- Chemical propulsion will remain the method of choice for many applications
- Novel chemical propellants offer great potential for near-term improvements

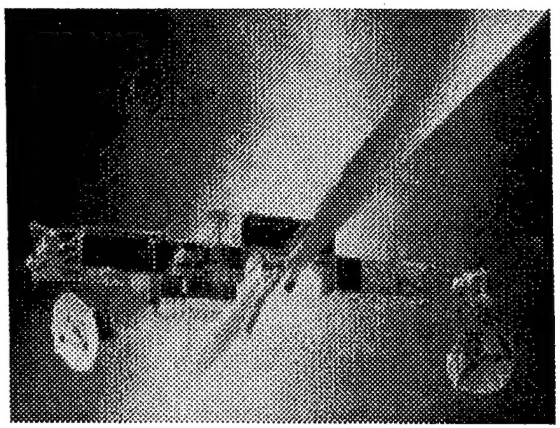
HEDM Program Objective

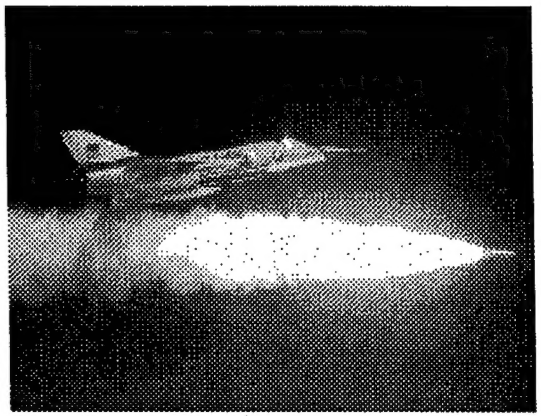


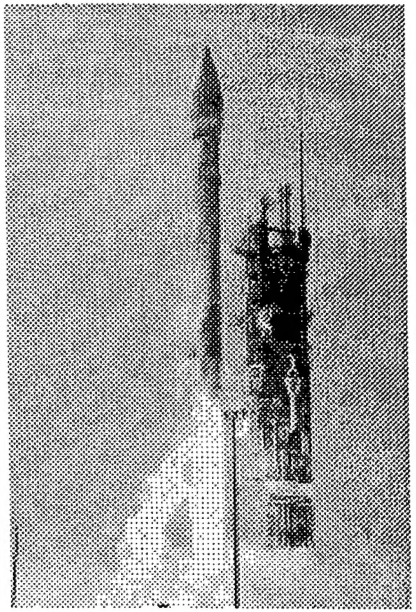
Breaking the performance barrier

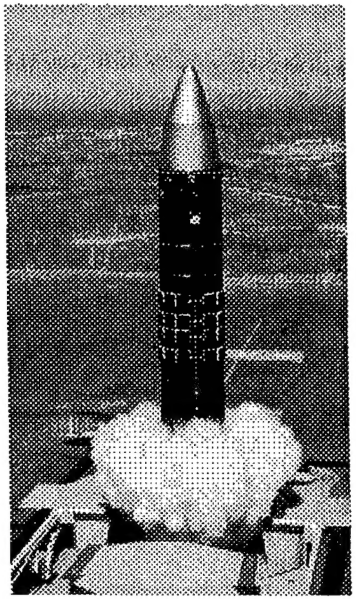
Identify and develop advanced chemical propellants for rocket propulsion applications

- Hydrocarbons for liquid boosters
- Liquid & solid oxidizers for boost and upper stages
- Monopropellants for upper stages and satellites
- Cryogenic propellants for upper stages









Assessment of energy density: Specific Impulse (I_{sp})

I_{sp} = pounds of delivered thrust / (pounds of propellant burned/second); similar to mpg.

$$I_{sp} \propto \sqrt{\Delta H_{comb} / m_{products}}$$

=> highly exothermic reactions AND combustion products with small masses are required

($\approx$ 50% of liquid H_2 in SSME is not burned!)

Specific impulse values of currently used propellants

Solid propellant: Ammonium perchlorate(AP)/Al powder/hydroxy-terminated polybutadiene (HTPB)

I_{sp} = 267 sec

Liquid propellant: RP-1/LOX

I_{sp} = 300 sec

Monopropellant: Hydrazine (N_2H_4)

I_{sp} = 230 sec

Cryogenic propellants: LH_2/LOX

I_{sp} = 390 sec

HEDM Propellant Payoffs

- Larger payloads, smaller vehicles, and lower launch costs
- Greater capability to access and exploit space

Vehicle Type	Baseline Vehicle	Propellant	Takeoff Mass (lb)	Payload Mass (lb)	Payload Mass (lb) With 10% Isp Increase
Two-stage ELV	Atlas II // Centaur D-1A	RP-1/LOX (Isp = 295 s) // LH2/LOX (Isp = 455 s)	360,000	12,500	15,600 **(+25%)**
SSTO RLV	Lockheed SSTO	LH2/LOX (Isp = 455 s)	1,900,000	40,000	68,000 **(+70%)**
Missile Defense Interceptor	Boost-Phase Interceptor	HTPB/Al/HMX (Isp = 270 s)	1,847	74	110 **(+49%)**

Our research is aimed at increasing propellant Isp by 5 to 50%

Computational chemistry plays an important role in identification and characterization of HEDM

Experimental synthesis and characterization is difficult

- Little or no intuition to guide synthesis of new molecules.

- Energetic compounds are thermodynamically (and often kinetically) unstable.

- Synthesis is time-consuming, expensive, high-risk.

Energetic compounds present several challenges to theory

Exotic electronic structures

- Large non-dynamical correlation effects => single configuration methods may not be applicable.

- Multiple potential energy surfaces (e.g., low-lying triplet state(s) often intersect the lowest singlet state.)

- Nonadiabatic interactions (e.g., spin-orbit coupling, radiationless transitions)

Which theoretical method(s) give reliable predictions?

Density Functional Theory

- Widely used due to its efficiency and accuracy (generally comparable to MP2.)

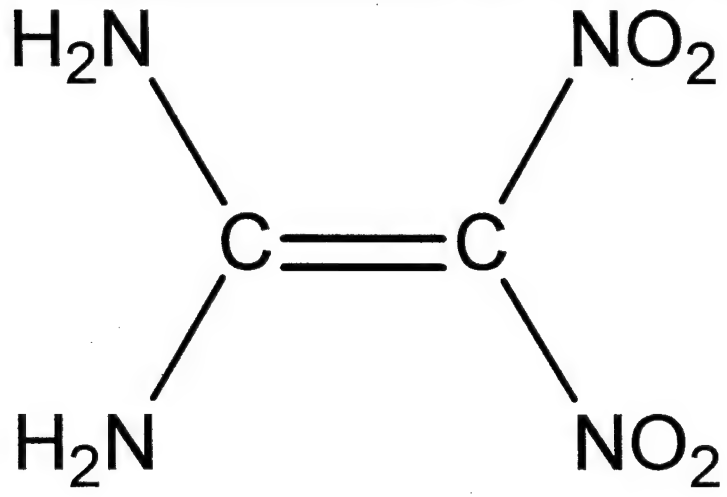
Single-configuration correlated methods

- MPn, CC, QCI, G2

Multiconfigurational methods

- MCSCF, MCQDPT, MRCI, MRCC

FOX-7: A prototypical energetic compound



I_{sp} = 254 sec (calculated)
ΔH_f = -9.5 kcal/mol (G2(MP2))

Advantages:

- Chemically balanced wrt decomposition products ($2CO + 2H_2O + 2N_2$)

- Lower impact/shock sensitivity than other $C_nH_{2n}O_{2n}N_{2n}$ compounds (e.g., RDX and HMX).

Recent Studies of FOX-7

Experimental X-ray structure

U. Bemm and H. Östmark, Acta Cryst. C54, 1997(1998).

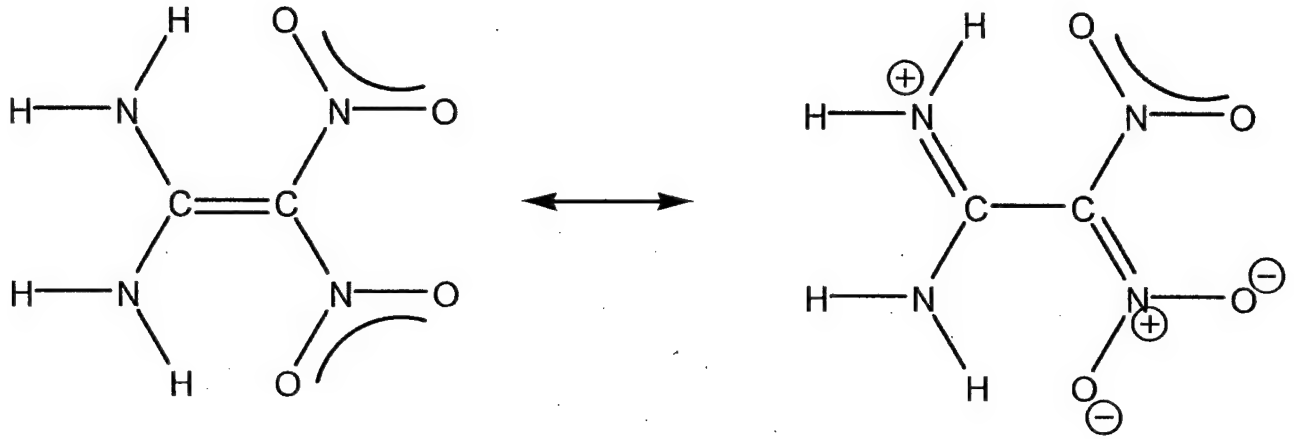
Structures and C-N bond energies (B3P86/6-31+G(d,p))

P.Politzer, M.C.Concha, M.E.Grice, J.S.Murray, P.Lane, and D.Habibollazadeh Theochem, 452, 75(1998)

Decomposition mechanisms (B3P86/6-31+G(d,p), B3LYP/6-31+G(d,p))

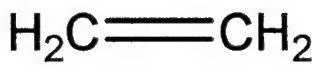
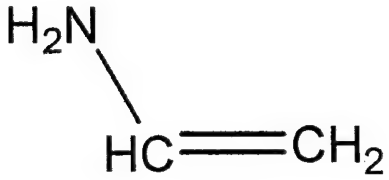
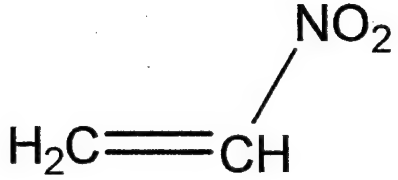
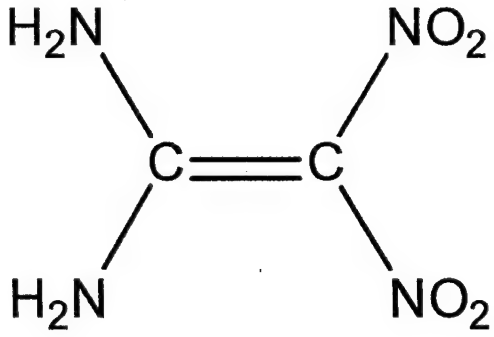
A.Gindulyte, L.Massa, L.Huang, and J.Karl, J. Phys. Chem. A, 103, 11045(1999)

FOX-7: A "Push-Pull" Ethylene



Multiple Lewis structures suggest that FOX-7 may have high degree of multiconfigurational character => good testbed for SOTA single-reference methods and DFT.

DFT Geometries

	C=C	C-NH_2	C-NO_2
	**1.331***		
	1.327		
	**1.340***	**1.386***	
	1.336	**1.392**	
	**1.326***		**1.459***
	1.322		**1.473**
	**1.426***	**1.339***	**1.424***
	1.428**	**1.345****	**1.432****
	1.421	**1.345**	**1.438**
	(1.456)	**(1.319, 1.325)**	**(1.399, 1.426)**

* P.Politzer, M.C.Concha, M.E.Grice, J.S.Murray, P.Lane, and D.Habibollazadeh Theochem, 452, 75(1998)

** A.Gindulyte, L.Massa, L.Huang, and J.Karl, J. Phys. Chem. A, 103, 11045(1999)

( ) U. Bemm and H. Östmark, Acta Cryst. C54, 1997(1998).

Approach

1. Compute C-NH_2 and C-NO_2 bond dissociation energies of FOX-7 and simpler prototypes using DFT (B3LYP), single-reference methods (MP2, G2(MP2), CCSDT//MP2), and a multireference method (MCQDPT(2)//CASSCF). 6-311G(d,p) used throughout.

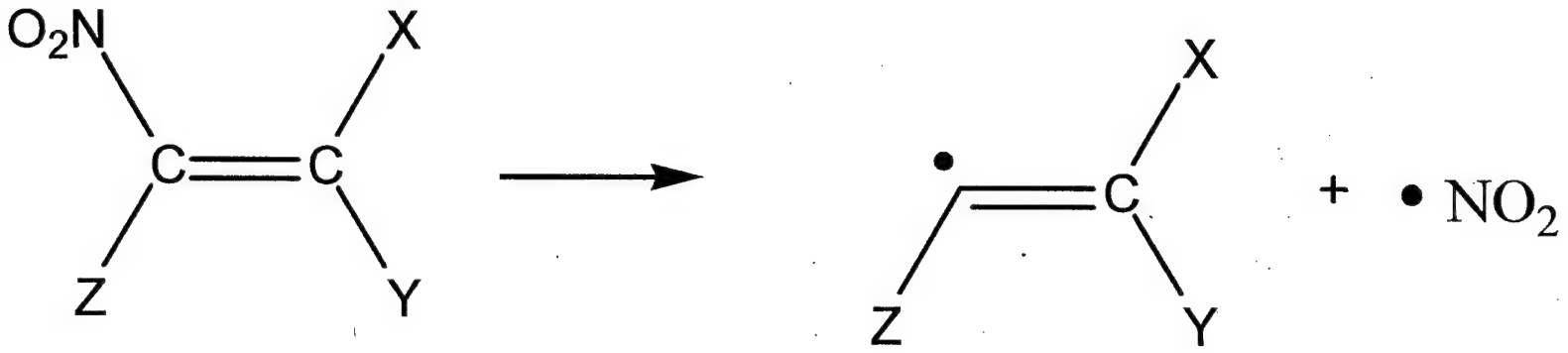
2. Assess degree of multiconfigurational character via calculation of natural orbital occupation numbers (MP2, CCSD(T), MCSCF).

- MP2 and CCSD(T) "non-physical" occupation numbers indicative of significant degree of multiconfigurational character

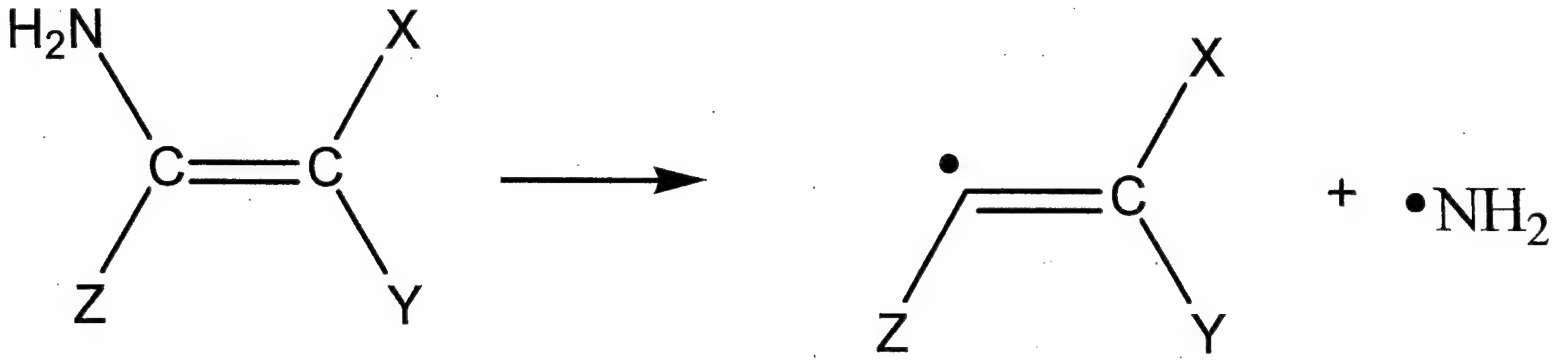
M.S. Gordon, M.W. Schmidt, G.M. Chaban, K. R. Glaesemann, W.J. Stevens, and C. Gonzalez, J. Chem. Phys., 110, 4199 (1999).

Bond Dissociation Reactions

C-NO_2 BDEs: X,Y = H, NH_2 ; Z = H, NO_2



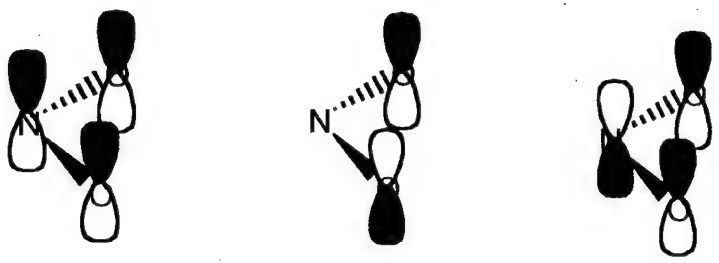
C-NH_2 BDEs: X,Y = H, NO_2 ; Z = H, NH_2



Choice of CASSCF Active Space

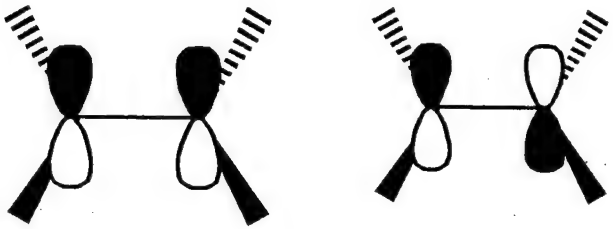
"Push-pull" Lewis structures suggest that delocalization of π electrons account for the most important non-dynamical correlation.

NO_2 (4e,3o)



π non-bonding π*

C-C (2e,2o)



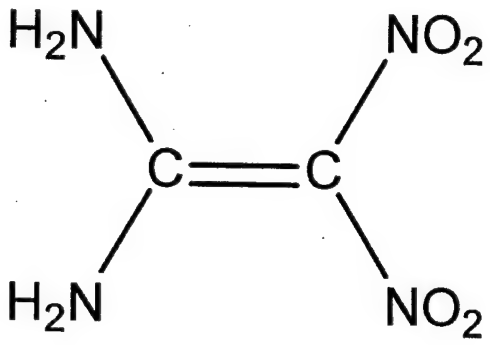
π π*

NH_2 (2e,1o)

C-N (2e,2o)

σ σ*

Structures of FOX-7



* P.Politzer, M.C.Concha, M.E.Grice, J.S.Murray, P.Lane, and D.Habibollazadeh Theochem, 452, 75(1998)

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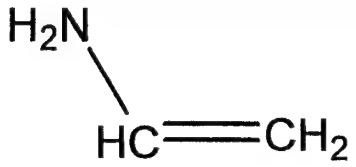
( ) U. Bemm and H. Östmark, Acta Cryst. C54, 1997(1998).

Level of theory	C=C	C-NH_2	C-NO_2
B3P86/6-31+G(d,p)	1.426*	1.339*	1.424*
B3LYP/6-31+G(d,p)	1.428**	1.345**	1.432**
B3LYP/6-311G(d,p)	1.421	1.345	1.438
MP2/6-311G(d,p)	1.392	1.359	1.441
CASSCF/6-311G(d,p)			
X-ray structure	(1.456)	(1.319) (1.325)	(1.399) (1.426)

Natural Orbital Occupation Numbers

(closed shell species)

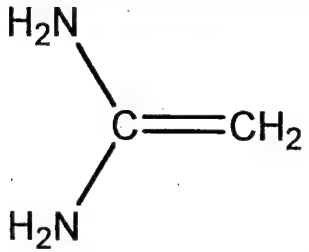


MP2: none

CCSD(T): none

⟨---------- **MCSCF (6e,5o)** ----------⟩

C=C	**π**	**π***
	1.927	0.079
C-NH$_2$	**σ**	**σ***
	1.980	0.020
NH$_2$ lp	1.994	



MP2: -0.001

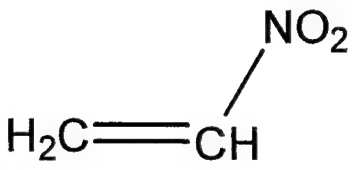
CCSD(T): none

⟨---------- **MCSCF (8e,7o)** ----------⟩

C=C	**π**	**π***
	1.940	0.068
C-NH$_2$	**σ**	**σ***
	1.978	0.023
	1.981	0.019
NH$_2$ lp	1.995	

Natural Orbital Occupation Numbers

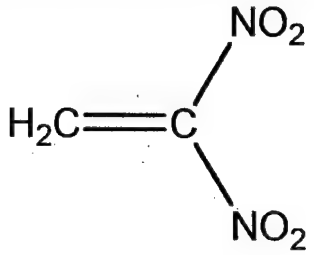
(closed shell species)



MP2: 2.00001, -0.00009

CCSD(T): none

⟨---------- MCSCF (8e,7o) ----------⟩			
C=C	π	π*	
	1.914	0.077	
NO_2	π	**n.b.**	π*
	1.983	1.897	0.130
C-NO_2	σ	σ*	
	1.977	0.023	



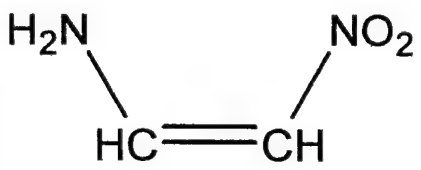
MP2: -0.001

CCSD(T): none

⟨---------- MCSCF (14e,12o) ----------⟩			
C=C	π	π*	
	1.915	0.077	
NO_2	π	**n.b.**	π*
	1.984	1.889	0.132
	1.984	1.883	0.137
C-NO_2	σ	σ*	
	1.977	0.030	
	1.973	0.020	

Natural Orbital Occupation Numbers

(closed shell species)

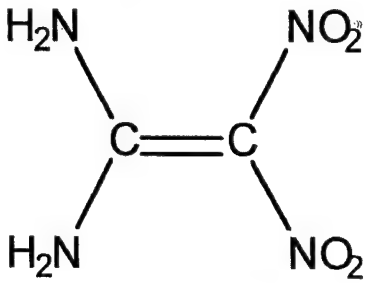


MP2: -0.00001(2)

CCSD(T): none

⟨--------- **MCSCF (12e,10o)** ----------⟩

C=C	π	π*	
	1.950	0.059	
NO_2	π	**n.b.**	π*
	1.983	1.914	0.108
C-NH_2	σ	σ*	
	1.981	0.019	
C-NO_2	σ	σ*	
	1.978	0.023	
NH_2 lp	1.987		



MP2: 2.00001(3), -0.00016, -0.00009, -0.00004, -0.00001

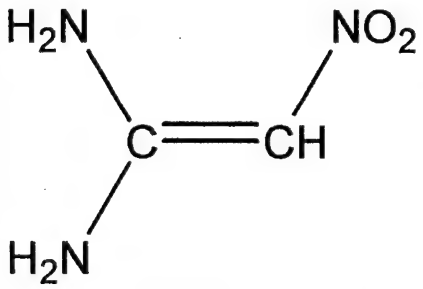
CCSD(T): none

⟨--------- **MCSCF (18e,14o)** ----------⟩

C=C	π	π*	
	1.983	0.036	
NO_2	π	**n.b.**	π*
	1.986	1.911	0.099
	1.989	1.906	0.113
C-NH_2	σ	σ*	
	1.982	0.018	
	1.978	0.022	
C-NO_2	σ	σ*	
	----- n/a -----		
NH_2 lp	1.988(2)		

Natural Orbital Occupation Numbers

(closed shell species)

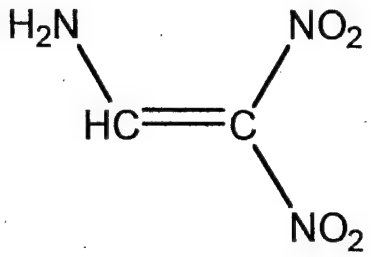


MP2: -0.0001(2)

CCSD(T): none

⟨---------- **MCSCF (16e,13o)** ----------⟩

C=C	π	π*	
	1.962	0.050	
NO_2	π	**n.b.**	π*
	1.983	1.921	0.100
C-NH_2	σ	σ*	
	1.982	0.018	
	1.977	0.022	
C-NO_2	σ	σ*	
	1.979	0.024	
NH_2 lp	1.994		
	1.990		



MP2: -0.0002(2), -0.00001

CCSD(T): none

⟨---------- **MCSCF (18e,15o)** ----------⟩

C=C	π	π*	
	TBD		
NO_2	π	**n.b.**	π*
	TBD		
C-NH_2	σ	σ*	
	TBD		
C-NO_2	σ	σ*	
	TBD		
NH_2 lp	TBD		

Natural Orbital Occupation Numbers

(open shell species)

$\bullet NH_2$

MP2: none

CCSD(T): none

⟨---------- **MCSCF (3e,2o)** ----------⟩

NH_2 lp	2.000
N rad.	1.000

$\bullet NO_2$

MP2: 2.00001

CCSD(T): none

⟨---------- **MCSCF (5e,4o)** ----------⟩

NO_2	**π**	**n.b.**	**π***
	1.986	1.937	0.078
N rad.	1.000		

MP2: 2.07575, -0.08353

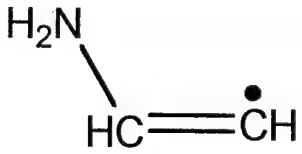
CCSD(T): none

⟨---------- **MCSCF** ----------⟩

C=C	**π**	**π***
	1.899	0.101
C rad.	1.000	

Natural Orbital Occupation Numbers

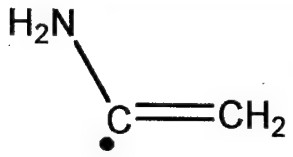
(open shell species)



MP2: 2.06629, -0.08353

CCSD(T): none

⟨---------- MCSCF (7e,6o) ----------⟩		
C=C	π	π*
	1.911	0.094
C-NH_2	σ	σ*
	1.980	0.021
NH_2 lp	1.995	
C **rad.**	1.000	



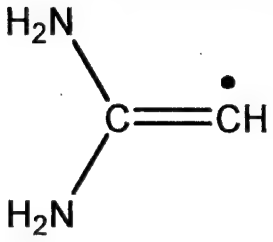
MP2: TBD

CCSD(T): TBD

⟨---------- MCSCF (7e,6o) ----------⟩		
C=C	π	π*
	1.918	0.084
C-NH_2	σ	σ*
	1.981	0.019
NH_2 lp	1.993	
C **rad.**	1.006	

Natural Orbital Occupation Numbers

(open shell species)

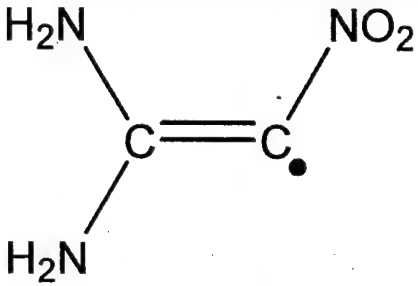


MP2: 2.04703, 2.00001, -0.06203, -0.00003

CCSD(T): none

⟨---------- **MCSCF (11e,9o)** ----------⟩

C=C	**π**	**π***
	1.924	0.083
C-NH$_2$	**σ**	**σ***
	1.977	0.023
	1.980	0.020
NH$_2$ lp	1.994	
	1.997	
C **rad.**	1.001	



MP2: TBD

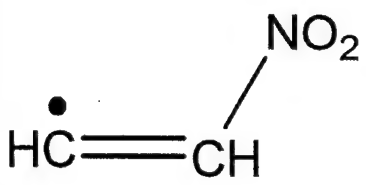
CCSD(T): TBD

⟨---------- **MCSCF (13e,12o)** ----------⟩

C=C	**π**	**π***	
	1.929	0.068	
NO$_2$	**π**	**n.b.**	**π***
	1.9834	1.907	0.114
C-NH$_2$	**σ**	**σ***	
	1.982	0.017	
	1.980	0.020	
C-NO$_2$	**σ**	**σ***	
	1.977	0.024	
NH$_2$ lp	**--- n/a ---**		

Natural Orbital Occupation Numbers

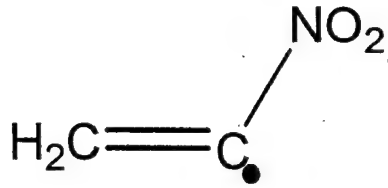
(open shell species)



MP2: 2.08805, 2.00001, -0.00001, -0.00006

CCSD(T): none

〈---------- MCSCF (9e,8o) ----------〉			
C=C	π	π*	
	1.904	0.083	
NO_2	π	**n.b.**	π*
	1.983	1.900	0.134
C-NO_2	σ	σ*	
	1.975	0.025	
C **rad.**	1.000		



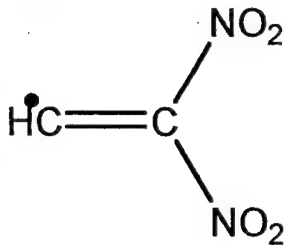
MP2: 2.09302, 2.00001, -0.00008, -0.10792

CCSD(T): TBD

〈---------- MCSCF (9e,8o) ----------〉			
C=C	π	π*	
	1.896	0.090	
NO_2	π	**n.b.**	π*
	1.983	1.891	0.141
C-NO_2	σ	σ*	
	1.977	0.023	
C **rad.**	1.000		

Natural Orbital Occupation Numbers

(open shell species)

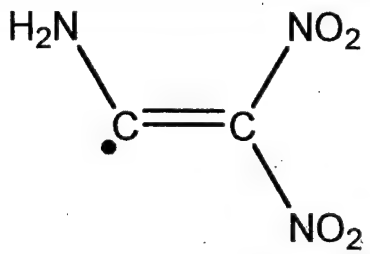


MP2: 2.08603, 2.00001(2), -0.10207, -0.00003

CCSD(T): TBD

⟨---------- **MCSCF (15e,13o)** ---------⟩

C=C	**π**	**π***	
	1.904	0.084	
NO_2	**π**	**n.b.**	**π***
	1.984	1.882	0.142
	1.984	1.888	0.133
C-NO_2	**σ**	**σ***	
	1.972	0.031	
	1.976	0.021	
C rad.	1.000		



MP2: 2.00001(2), -0.0013, -0.00055

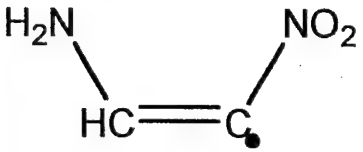
CCSD(T): none

⟨---------- **MCSCF (15e,12o)** ---------⟩

C=C	**π**	**π***	
	1.976	0.043	
NO_2	**π**	**n.b.**	**π***
	1.989	1.905	0.114
	1.987	1.909	0.103
C-NO_2	**σ**	**σ***	
	---- n/a ----		
C-NH_2	**σ**	**σ***	
	1.981	0.020	
NH_2 lp	1.974		
C rad.	1.000		

Natural Orbital Occupation Numbers

(open shell species)

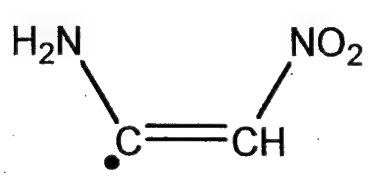


MP2: 2.05145, 2.00001, -0.00014, -0.06755

CCSD(T): TBD

⟨---------- **MCSCF (13e,11o)** ---------⟩

C=C	**π**	**π***	
	1.923	0.079	
NO_2	**π**	**n.b.**	**π***
	1.983	1.906	0.119
C-NO_2	**σ**	**σ***	
	1.977	0.024	
C-NH_2	**σ**	**σ***	
	1.979	0.019	
NH_2 lp	1.990		
C rad.	1.001		



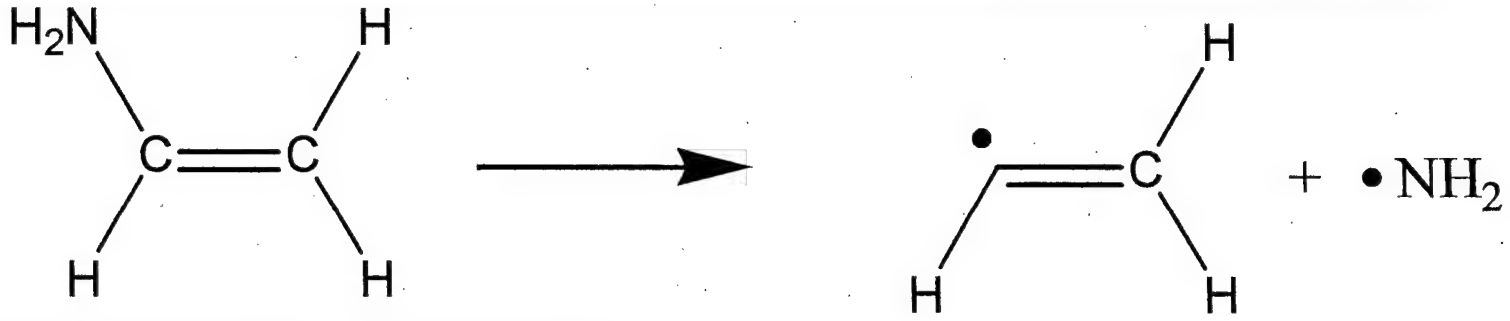
MP2: 2.00001, -0.00002, -0.00015, -0.01124

CCSD(T): TBD

⟨---------- **MCSCF (13e,11o)** ---------⟩

C=C	**π**	**π***	
	1.938	0.064	
NO_2	**π**	**n.b.**	**π***
	1.982	1.911	0.112
C-NO_2	**σ**	**σ***	
	1.976	0.025	
C-NH_2	**σ**	**σ***	
	1.980	0.019	
NH_2 lp	1.987		
C rad.	1.006		

C-NH_2 Bond Dissociation Energies (kcal/mol)



DFT	105.2 109.8 (103.3)*
MBPT(2)	115.6
G2(MP2)	110.8 (102.4)
CCSD(T)//MBPT(2)	104.7
MCQDPT(2)//MCSCF	101.9
experiment†	102

•NH_2

----- Non-physical NOONS ----		---- MCSCF ---
MBPT(2)	CCSD(T)	
none	none	n/a

•$CH{=}CH_2$

----- Non-physical NOONS ----		---- MCSCF(3e,3o) ---		
MBPT(2)	CCSD(T)	C=C	π	π*
2.07575	none		1.899	0.101
-0.09409		C rad.	1.000	

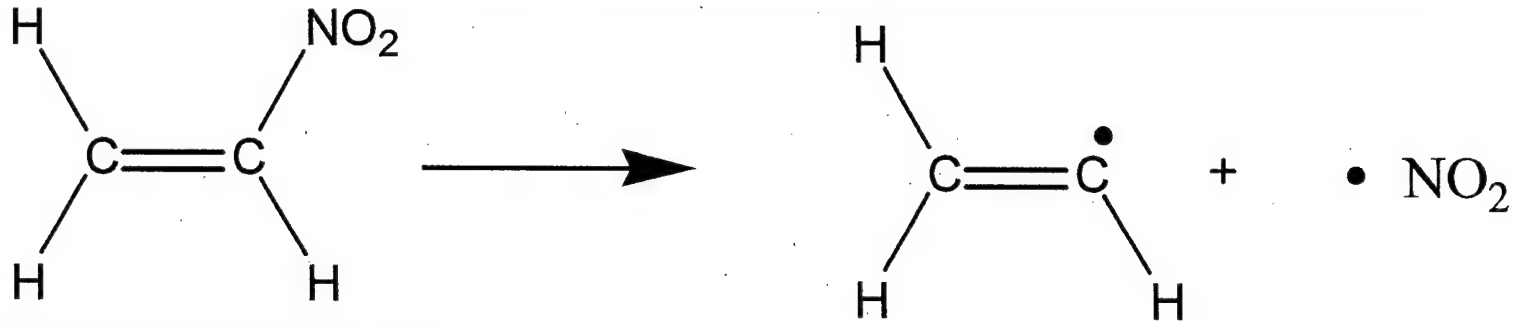
$NH_2CH{=}CH_2$

----- Non-physical NOONS ----		---- MCSCF(6e,5o) ---		
MBPT(2)	CCSD(T)	C=C	π	π*
none	none		1.927	0.079
		NH_2 lp	1.994	
		C-NH_2	σ	σ*
			1.980	0.020

* P.Politzer, M.C.Concha, M.E.Grice, J.S.Murray, P.Lane, and D.Habibollazadeh Theochem, 452, 75(1998). Values in () include ZPE corrections.

† S.G.Lias, J.E.Bartmess, J.F. Liebman, J.L.Holmes, R.D. Levin, W.G.Mallard, J. Phys. Chem. Ref. Data 17 (Suppl. 1), 1988.

C-NO_2 Bond Dissociation Energies (kcal/mol)



DFT	68.8
	74.5*
MBPT(2)	77.7
G2(MP2)†	79.4
CCSD(T)//MBPT2	70.9
MCQDPT(2)//MCSCF	59.5

$\bullet NO_2$

----- Non-physical NOONS ----

MBPT(2)	CCSD(T)
2.00001	none

---- MCSCF(5e,4o) ---

NO_2	π	n.b.	π*
	1.986	1.937	0.078
N rad.		1.000	

$\bullet CH{=}CH_2$

----- Non-physical NOONS ----

MBPT(2)	CCSD(T)
2.07575	none
-0.09409	

---- MCSCF(3e,3o) ---

C=C	π	π*
	1.899	0.101
C rad.	1.000	

$NO_2CH{=}CH_2$

----- Non-physical NOONS ----

MBPT(2)	CCSD(T)
2.00001	none
-0.00009	
-0.00004	

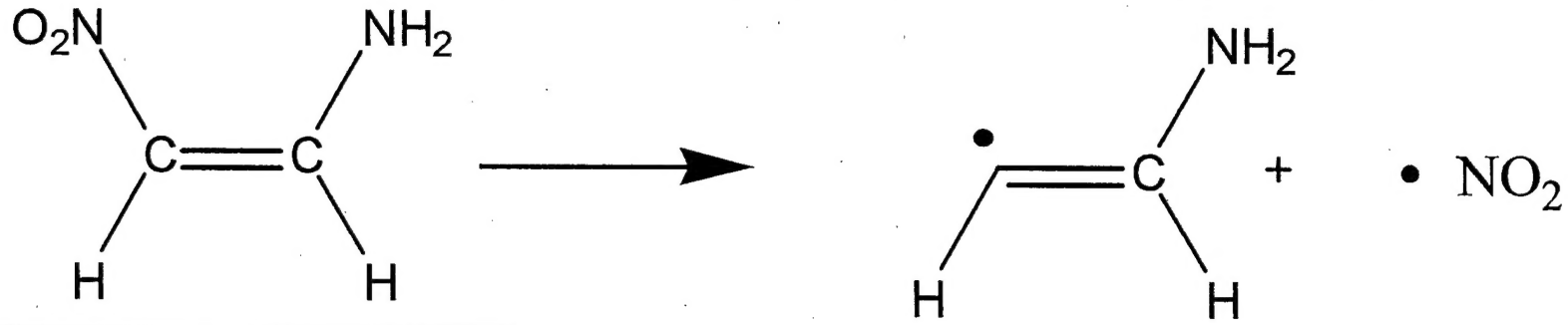
---- MCSCF(8e,7o) ---

C=C	π	π*
	1.914	0.077
NO_2	π	n.b. π*
	1.983	1.897 0.130
C-NO_2	σ	σ*
	1.977	0.023

* P.Politzer, M.C.Concha, M.E.Grice, J.S.Murray, P.Lane, and D.Habibollazadeh Theochem, 452, 75(1998).

† Does not include ZPE corrections.

C-NO_2 Bond Dissociation Energies (kcal/mol)



DFT	81.4 88.0*
MBPT(2)	86.2
G2(MP2)†	88.8
CCSD(T)//MBPT2	78.2
MCQDPT(2)//MCSCF	66.7

•NO_2

----- Non-physical NOONS ----

MBPT(2)	CCSD(T)
2.00001	none

---- MCSCF(5e,4o) ---

NO_2	π	n.b.	π*
	1.986	1.937	0.078
N rad.	1.000		

•CH=CH-NH_2

----- Non-physical NOONS ----

MBPT(2)	CCSD(T)
2.06629	none
-0.08353	
-0.00001	

---- MCSCF(7e,6o) ---

C=C	π	π*
	1.911	0.094
C rad.	1.000	
NH_2 lp	1.995	

NO_2CH=CH-NH_2

----- Non-physical NOONS ----

MBPT(2)	CCSD(T)
2.00001	TBD
-0.00009	
-0.00004	

---- MCSCF(12e,10o) ---

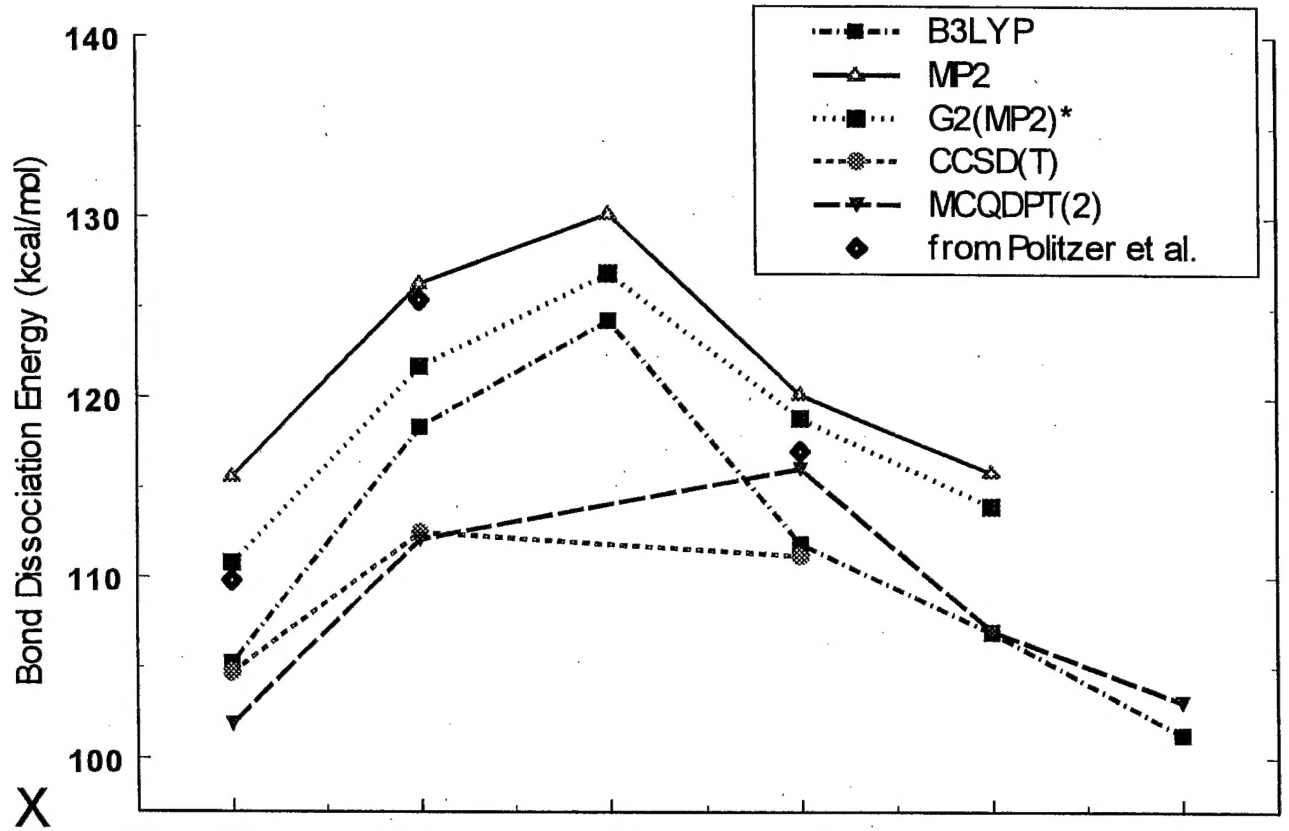
C=C	π	π*
	1.950	0.059

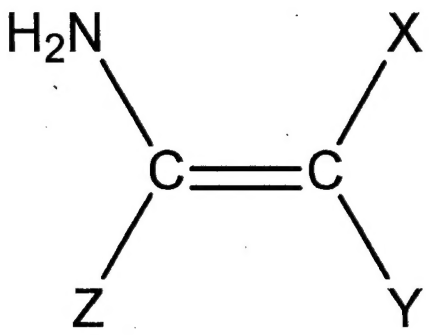
NO_2	π	n.b.	π*
	1.983	1.914	0.108
NH_2 lp	1.987		

* P.Politzer, M.C.Concha, M.E.Grice, J.S.Murray, P.Lane, and D.Habibollazadeh Theochem, 452, 75(1998).

† Does not include ZPE corrections.

C-NH_2 Bond Dissociation Energies (kcal/mol)





* does not include ZPE corrections

Summary and Conclusions

1. The C-NH_2 and C-NO_2 bond dissociation energies of FOX-7 and simpler prototypes have been computed using DFT (B3LYP), single-reference (SR) methods (MP2, G2(MP2), CCSD(T)//MP2), and a multireference (MR) method (MCQDPT(2)//CASSCF).

2. With the exception of aminoethylene and amino radical, all of the closed shell and radical species considered in this study have non-physical NOONs at the MP2 level.

3. CCSD(T) is better able to "capture" non-dynamical correlation than MP2.

4. Species containing a nitro group generally have a higher degree of multiconfigurational character than those without NO_2.

5. The DFT BDEs generally are in better agreement with the SR methods (MP2, G2(MP2), CCSD(T)) than with MCQPDT(2)), particularly for C-NO_2.

6. The MCQDPT(2) BDEs are lower than those of the SR methods. The difference between the SR and MR predictions is greater for C-NO_2 than C-NH_2.

7. The most stringent comparison of these methods will likely be the C-NO_2 BDE for $(NH_2)_2C{=}C(NO_2)_2$, for which the radical $(NH_2)_2C{=}C{-}NO_2$ is <u>exceptionally</u> MR in nature.

Future Directions

1. Include additional MR methods (MRCI, MRCC).
2. For the smaller systems, try larger basis sets (cc-pVTZ).
3. Replace UHF reference with ROHF for MP2, CCSD(T).

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AFOSR

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